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Cis-Selective Ring-Opening Metathesis Polymerization with Ruthenium Catalysts

Benjamin K. Keitz, Alexey Fedorov, and Robert H. Grubbs*

Arnold and Mabel Beckman Laboratories of Chemical Synthesis, Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California, 91125

Abstract

Using a C-H activated, ruthenium-based metathesis catalyst, the *cis* selective ROMP of several monocyclic alkenes, as well as norbornene and oxanorbornene-type monomers is reported. The *cis* content of the isolated polymers depended heavily on monomer structure and temperature. By lowering the temperature, *cis* content as high as 96% could be obtained.

Ring-opening metathesis polymerization (ROMP) is a powerful methodology for the preparation of a wide range of synthetic polymers including block,¹ brush,² and cyclic architectures.³ Furthermore, ROMP can also be used to prepare polymers with specific microstructures comprising various tacticities (e.g. atactic, isotactic, syndiotactic), double bond arrangements (*cis*/*trans*), or different relative monomer configurations (e.g. head to tail, head to head, etc.).⁴ Control of these microstructures is essential for preparing polymers with well-defined properties. For instance, higher content of *cis* double bonds (%*cis*) is typically associated with lower melting and glass transition temperatures while inducing slower rates of crystallization.^{5–7} Likewise, the properties of conjugated polymers can be adjusted by varying the percentage of *cis* double bonds they contain.⁸

Several metathesis catalysts, based on Re, Os, Mo, and W, have been shown to give high *cis* content in the ROMP of norbornene and norbornadiene derivatives.^{9,10} Many of these catalysts have also demonstrated an ability to generate polymers with well-defined tacticities. Although %*cis* varies significantly with catalyst, monomer, solvent,¹¹ and temperature,¹² Ru-based initiators, such as (PCy₃)₂Cl₂Ru=CHPh, give almost exclusively *trans* polymers.^{13,14} Indeed, this has been a serious limitation for previous generations of Ru-based metathesis catalysts, as highlighted by Schrock and coworkers.^{10c} The best literature examples of stereoselective ROMP with Ru catalysts include alternating copolymerization of norbornene with cycloalkenes to give polymers with up to 75% *cis* double bonds.^{15,16} Our group described similar %*cis* values for sulfonate and phosphate substituted NHC-based catalysts as well.¹⁷

We recently reported on a new class of Ru-based metathesis catalysts where the N-heterocyclic carbene (NHC) ligand is chelated to the metal center through a Ru-C bond formed via C-H activation.¹⁸ These catalysts showed remarkable selectivity for the formation of *cis* olefins during a wide variety of cross-metathesis reactions. Our initial ROMP experiments with the C-H activated catalysts revealed no significant increase in *cis* content compared to standard catalysts such as **1** (Figure 1). However, after having

Corresponding Author rhg@caltech.edu.

ASSOCIATED CONTENT

Supporting Information Full experimental details and NMR spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>

discovered the improved activity, stability, and selectivity of nitrato-complex **2**,¹⁹ we decided to investigate the ROMP behavior of this catalyst more closely. Herein, we show that the *cis*-selectivity of **2** extends to the ROMP of various monomers and consequently establish that Rubased metathesis catalysts are capable of forming polymers with high *cis* content. We also demonstrate that classic NHC-based Ru catalysts (e.g. **1**) can give polymers with unexpectedly high *cis* selectivity in certain situations.

When **2** was added to a solution of norbornene (**3**) in THF at room temperature (RT), an immediate increase in the viscosity of the solution occurred. Isolation of the resulting polymer (**poly-3**) and subsequent characterization by ¹H and ¹³C NMR spectroscopy revealed that it contained ca. 88% *cis* double bonds (Figure 2).²⁰ In contrast, **poly-3** prepared using **1** showed %*cis* values of 58% (Table 1).²¹ These later values are typical of NHC-supported Ru-based metathesis catalysts. Importantly, an even higher selectivity of ca. 96% *cis* could be obtained with **2** by lowering the temperature of the monomer solution prior to the addition of the catalyst. This trend was also observed when norbornadiene (**4**) was reacted with **2** at different temperatures (Figure 3). The almost exclusive formation of *cis* **poly-4** with **2** is particularly noteworthy since **1** gave no detectable amount of the *cis* isomer.²² However, **poly-4** prepared with **2** was atactic, as evidenced by the lack of long-range order in the ¹³C NMR spectrum (see the Supporting Information).

Having established that **2** could furnish polymers with high *cis* content for both **3** and **4**, we turned our attention to more complex monomers. Many of these monomers have been polymerized with very high *cis* selectivity and tacticity control using Mo- and W-derived catalysts, but formed predominantly *trans* polymers when (PCy₃)₂Cl₂Ru=CHPh was used.¹³ Gratifyingly, we found that in almost every case, **2** yielded a polymer with high *cis* content approaching 90%. In the cases where *cis*-selectivity with **2** at RT was below that value, conducting ROMP at -20 °C increased %*cis* by 6–15% (Table 1). In general a lower fraction of *cis* double bonds was observed for polymers prepared using **1**. However, in the case of monomers **5**, **6**, and **9**, high *cis* content was achieved without the use of a specially designed catalyst! This is particularly surprising since the closely analogues (PCy₃)₂Cl₂Ru=CHPh is known to give **poly-5** with only 11% *cis* double bonds.¹³ In contrast to **poly-5** and **poly-9** prepared by Mo-based catalysts,¹⁰ no long-range order was observed using either of the Ru-based initiators. With **2**, the formation of atactic polymers can be explained by fast carbene epimerization relative to the rate of propagation. This result is typical of Ru-based catalysts, and only under special circumstances is tacticity control achieved.^{14,23}

Experimental molecular weights (M_n) for polymers prepared with **2** were generally higher than the predicted values, which is indicative of incomplete catalyst initiation or a high rate of propagation (k_p) relative to the rate of initiation (k_i). This could be qualitatively observed as a solution of **2** and **3** remained purple (the color of **2**), even after complete conversion of the monomer. Based on the relatively low initiation rate constant of **2**, this result was expected.²⁴

In contrast to norbornene and norbornadiene-type monomers, cyclooctadiene (COD, **12**), cyclopentene (**13**), and *cis*-cyclooctene (**14**) are significantly more difficult to polymerize via ROMP due to their lower ring-strain.²⁵ Furthermore, the *Z*-selective ROMP of these monomers is particularly challenging due to the prevalence of intra- and intermolecular chain-transfer reactions and secondary metathesis events.^{4,26} In fact, the *Z*-selective ROMP of **12** has only recently been reported using a Mo metathesis catalyst.^{10a,27} Given the strong preference of **2** for *cis*-selective polymerization of bicyclic monomers, the next logical step was to attempt the ROMP of more difficult substrates, such as **12–14**.

When **12** was exposed to **2** (1 mol%) in C₆D₆ (0.6 mL), only minimal conversion (<20%) was observed after 24 h at RT. Surprisingly, increasing the temperature did not result in higher conversions, despite the fact that no catalyst decomposition was observed by ¹H NMR spectroscopy. Increasing the substrate concentration and switching the solvent to THF also did not increase the conversion of **12**, nor did repeating the reaction in neat **12**. However, polymerizing **12** with **2** in THF at RT over a period of 3 days provided a modest amount of **poly-12** (19% yield). Isolation and subsequent analysis of **poly-12** via ¹³C NMR spectroscopy revealed that it contained 96% *cis* double bonds, a value comparable to that obtained with the Mo-based system (Table 2). Similar to the ROMP of **3** and **4**, increasing the temperature of the polymerization of **12** resulted in polymers with lower *cis* content, although it never went below 80%. The extraordinariness of the above result is highlighted by the fact that **1** yielded **poly-12** with 90% *trans* selectivity.²⁶

Subsequent to our experiments with **12**, we found that **2** was also effective at polymerizing **13**, although the isolated yield of **poly-13** was still low (Table 2). Characterization of **poly-13** by ¹³C NMR spectroscopy revealed 48% *cis* content, which is significantly lower than the *cis* content of **poly-12** prepared by **2**. Similar levels of *cis* selectivity have been reported in copolymerizations with **3**, although these generally resulted from incomplete incorporation of **13**.^{15d} Switching to **1** produced **poly-13** with only 15% *cis* double bonds. Thus, the use of **2** resulted in a significant improvement in the %*cis* of **poly-13**, albeit to a lesser extent than was anticipated.

Unfortunately, no conversion of **14** was observed when it was exposed to **2** under a variety of conditions.²⁸ This was surprising since the strain energy of **14** (7.4 kcal/mol) is greater than that of **13** (6.8 kcal/mol).²⁵ Nevertheless, we reasoned that a more significant increase in strain energy, resulting from the use of *trans*-cyclooctene (**15**), would provide access to the desired polymer.²⁹ Indeed, reaction of **2** with **15** at RT in THF resulted in the immediate and high yielding production of **poly-15**. Characterization of this polymer revealed a *cis* content of 70%, a value that is among the highest reported for ruthenium-based catalysts.³⁰ Notably, **poly-15** prepared from **1** contained ~82% *trans* double bonds.

As mentioned above, secondary metathesis events are common in non-rigid polymers, because the active chain end is capable of intra – (“back-biting”) and intermolecular chain transfer reactions. Taking this into account, the *cis* selective polymerizations of **12**, **13**, and **15** with **2** are remarkable. Indeed, given the very high %*cis* of **poly-12** and no erosion of *cis* content over the course of polymerization, one should conclude that **2** is less prone to isomerizing or reacting with internal double bonds in polymers while displaying high kinetic selectivity for the formation of *cis* double bonds. Our molecular weight data also supports this argument, as **poly-12/13** prepared from **2** had much higher molecular weights compared to **poly-12/13** prepared from **1**. Such a result is consistent with a reduction in the number of chain transfer events, which tend to lower molecular weight.³¹ The importance of controlling secondary metathesis is reinforced by examination of the polymers prepared from **1**. In the case of **poly-5/6/9**, where secondary metathesis is suppressed due to steric effects, catalyst **1** yielded polymers with relatively high *cis* content. In contrast, **poly-12/13** have no protection against secondary metathesis and thus the thermodynamically favored *trans* olefin is eventually formed when these polymers are prepared from **1**. Although we have not specifically investigated the mechanistic origin of Z-selectivity in ROMP, calculations performed on an analogue of **2** indicate that steric pressure exerted by the NHC on side-bound ruthenacycles is responsible for the observed Z-selectivity during cross-metathesis.^{15c,32} It is likely that a similar mechanism is also responsible for the selectivities observed above.

In conclusion, we have demonstrated the *cis* selective ROMP of several monomers using Ru-based catalysts. The resulting polymers were recovered in moderate to high yield and *cis* content ranged from 48–96%. While the *cis* content varied significantly based on monomer structure, our C-H activated catalyst (**2**) gave polymers with significantly higher %*cis* values compared to those prepared by a more traditional Ru metathesis catalyst (**1**), while also showing qualitatively reverse stereoselectivity compared to (PCy₃)₂Cl₂Ru=CHPh. These results culminated in the highly *cis* selective polymerization of **12**, thereby proving that *cis* selective ROMP is possible with Ru catalysts, even with monomers that are prone to secondary metathesis. Future work in our laboratory will focus on improvements to both the activity and *cis* selectivity of **2**, with an emphasis on the application of this exciting new class of catalysts towards the development of novel polymer architectures.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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 20. In early metal metathesis systems, solvents such as dioxane have been shown to increase *cis* content (see ref. 13b). In the case of **2**, no change in *cis* content (for **poly-3**) was observed when the solvent was changed from THF to benzene, dioxane, or DME.
 21. The *cis* content of **poly-3** did not change when the structurally related (H₂IMes)Cl₂Ru(=CH-*o*-ⁱPr-Ph) and (H₂IMes)Cl₂Ru(C₅H₅N)₂ were used as catalysts in place of **1**. This should not be surprising since all three catalysts initiate to give the same propagating species.
 22. Lowering the temperature of polymerizations using **1** resulted in only a slight increase in %*cis* that was never more than 5%. See the Supporting Information for details.
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 24. The initiation rate constants of **1** and **2** are $4.6 \times 10^{-4} \text{ s}^{-1}$ and $8.4 \times 10^{-4} \text{ s}^{-1}$ respectively. Both these values are significantly smaller than the initiation rate constant of (H₂IMes)Cl₂Ru(C₅H₅N)₂ ($>0.2 \text{ s}^{-1}$), which is the preferred catalyst for ROMP. Note that the initiation rate constant of **2** depends on olefin concentration. See the following for a discussion of initiation in ruthenium metathesis catalysts: (a) Sanford MS, Love JA, Grubbs RH. *J. Am. Chem. Soc.* 2001; 123:6543. [PubMed: 11439041] (b) Love JA, Morgan JP, Trnka TM, Grubbs RH. *Angew. Chem. Int. Ed.* 2002; 41:4035.
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 28. Subsequent addition of norbornene to the reaction mixture containing **14** and **2** gives **poly-3** with the same selectivity as obtained in the individual polymerization of **3** with **2**, thus demonstrating that *cis*-cyclooctene does not decompose or inhibit **2**
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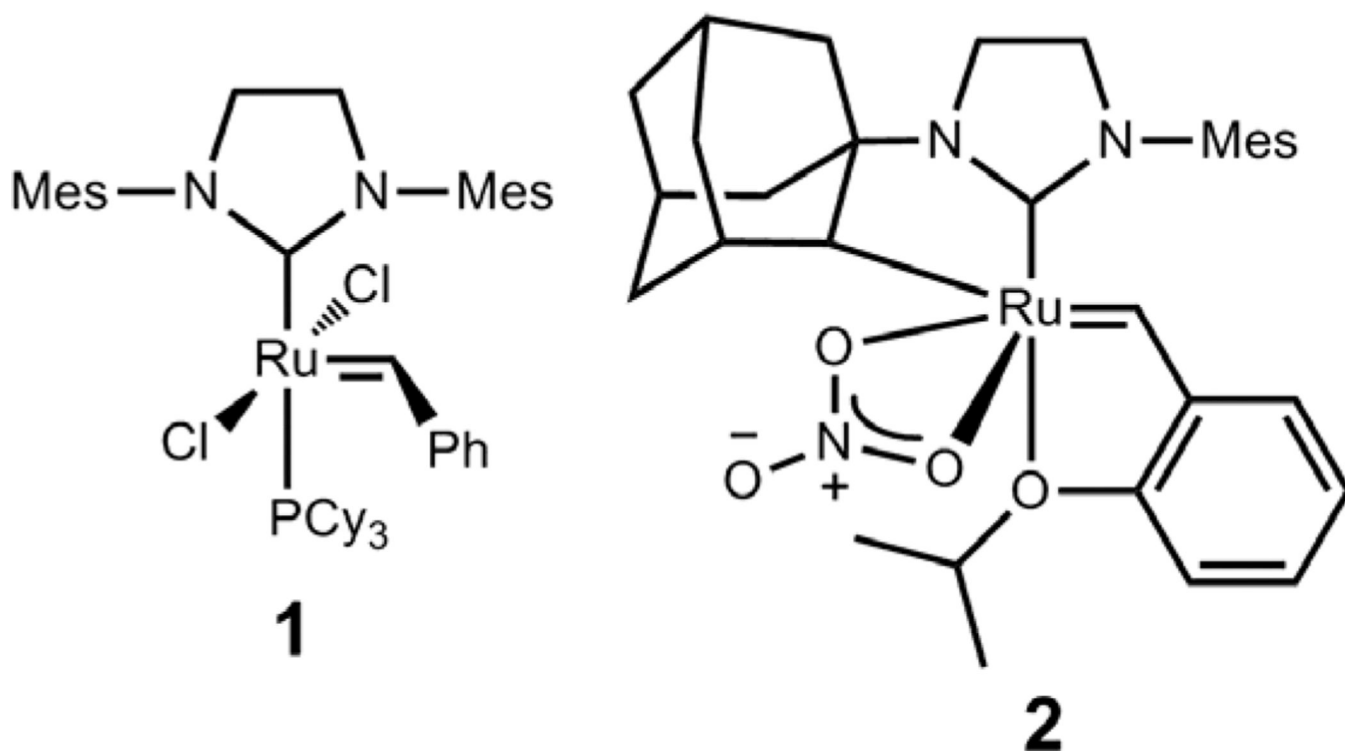


Figure 1.
Catalysts **1** and **2**. Mes = 2,4,6-trimethylphenyl.

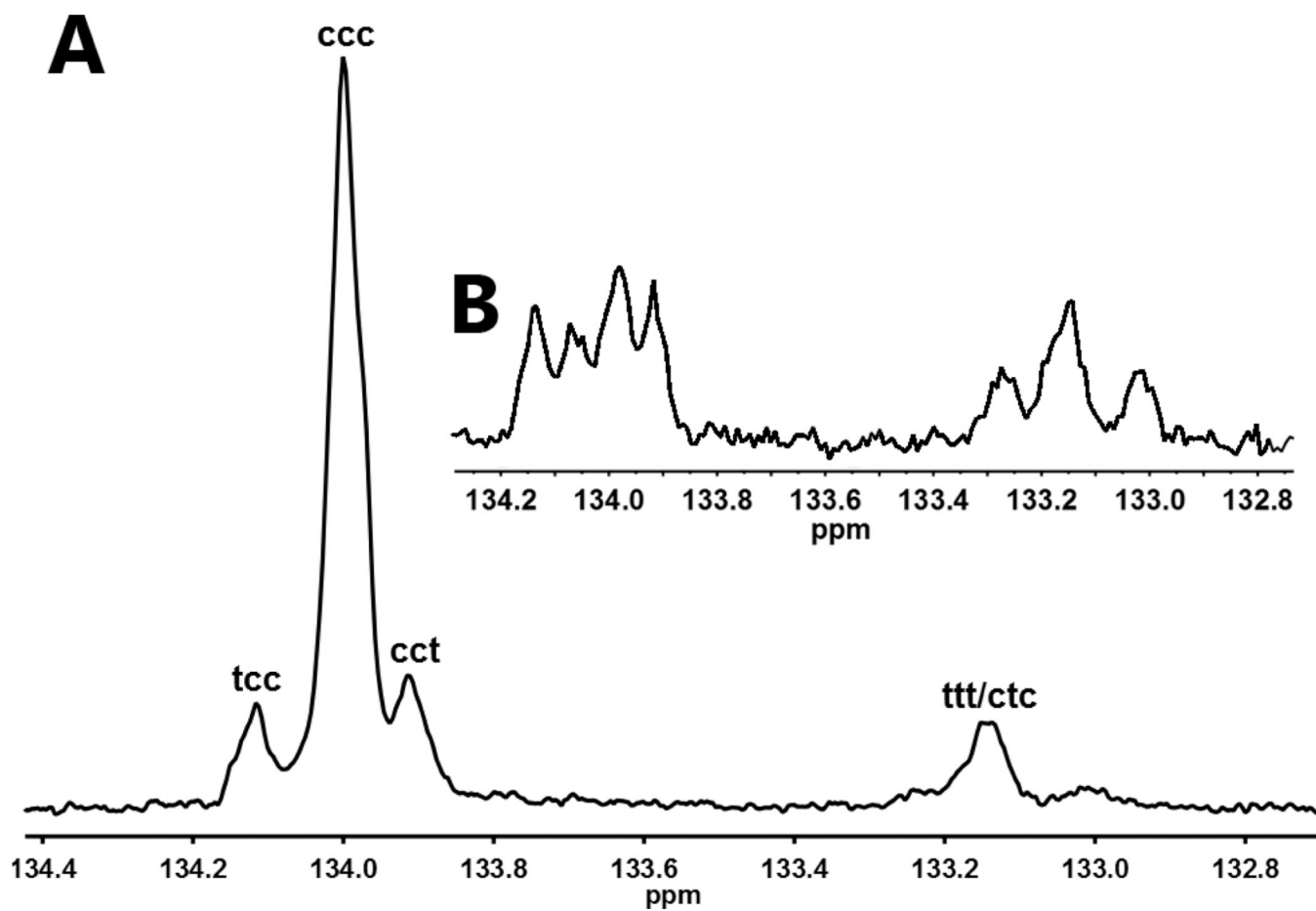


Figure 2.

(A) ^{13}C NMR spectrum (CDCl_3) of **poly-3** prepared from **3** (0.5 mmol) and **2** (0.005 mmol) in THF (2 mL) at RT. “ccc” and “cct” represent cis-cis-cis and cis-cis-trans triads consistent with literature reports.⁴ (B) ^{13}C NMR spectrum of **poly-3** prepared from **2**.

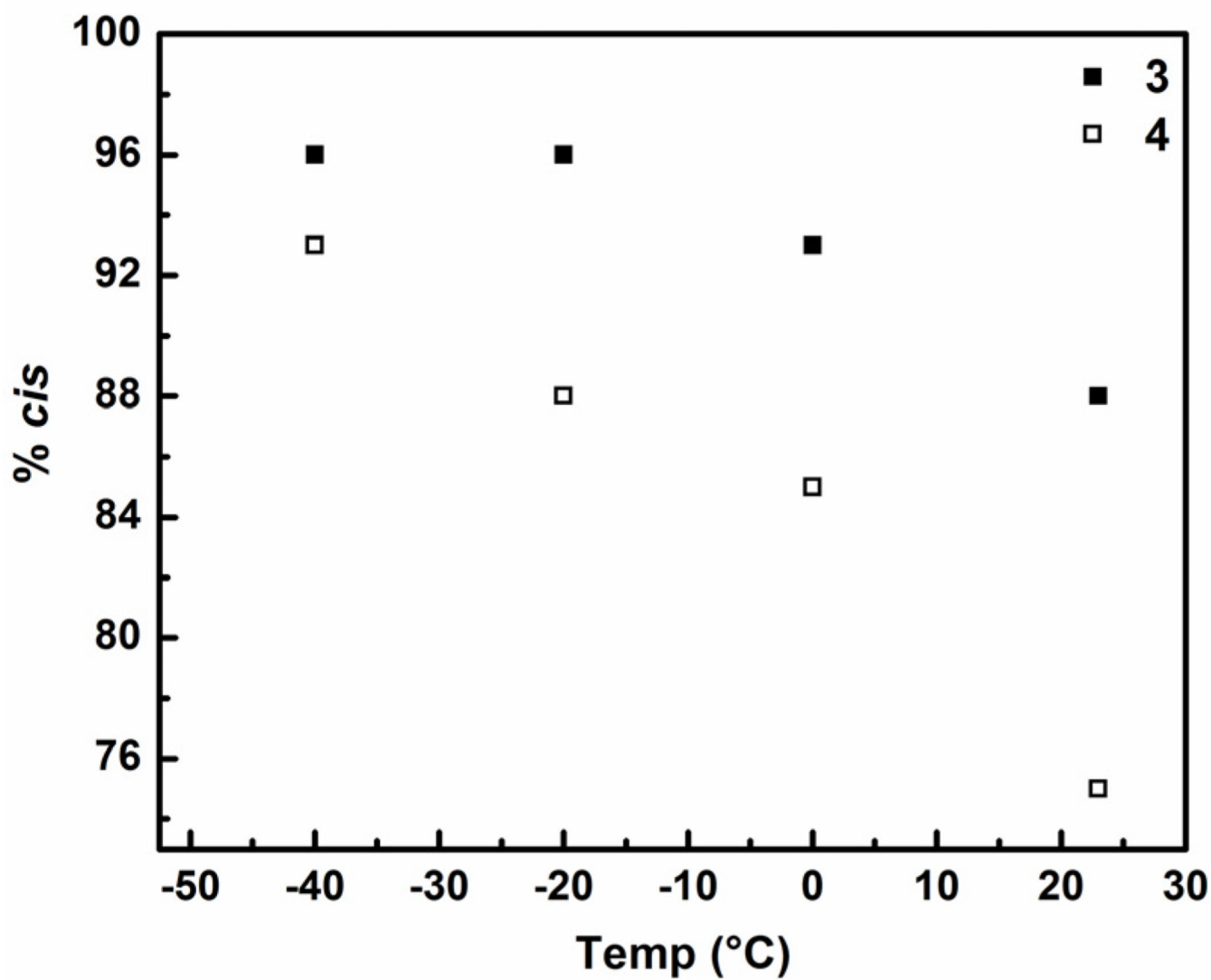
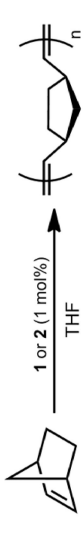
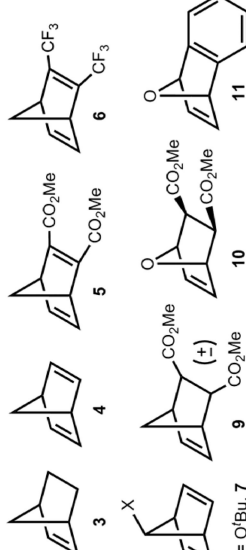


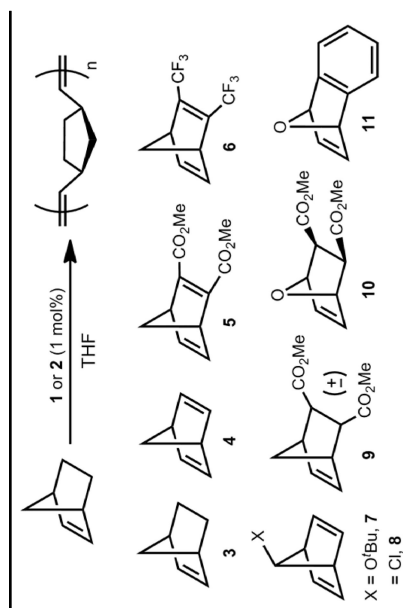
Figure 3.

Change in %*cis* with temperature for **poly-3** and **poly-4** polymerized with **2**. Conditions were monomer (0.5 mmol) and **2** (0.005 mmol) in THF (2 mL). *Cis* content was determined by ^1H NMR spectroscopy.

Table 1

Polymerization of **3–10** with catalysts **1** and **2**.^a

					
					
<p>X = O^tBu, 7 = Cl, 8</p>					
Monomer	Catalyst	Cis, ^b %	Yield, ^c %	M _n , ^d kDa	PDI ^d
3	1	58	88	112	1.65
	2	88	94	347	1.87
4	1	<5	93	— ^e	— ^e
	2	75	88	—	—
5	1	93	78	95.5	1.21
	2	86	91	—	—
6	1	78	95	179	1.24
	2	61	40	137	1.21
7	1	58	78	—	—
	2	84	73	—	—
8	1	50	64	144	1.08
	2	69	81	328	1.09
	2	80 ^f	79	—	—
9	1	81	95	484	1.49
	2	91	78	629	1.33
10	1	66	>95	463	1.5



Monomer	Catalyst	Cis, ^b %	Yield, ^c %	M _n , ^d kDa	PDI ^d
11	2	74	93	183	1.2
	2	80 ^f	79	—	—
	1	67	>95	—	—
	2	76	47	—	—
	2	91 ^{f,g}	80	—	—

^a Conditions were monomer (1 mmol) and catalyst (0.01 mmol) in THF (4 mL, 0.25 M) at RT.

^b Determined by ¹H NMR and ¹³C NMR spectroscopy.

^c Isolated yield.

^d Determined by multiangle light scattering (MALS) gel permeation chromatography (GPC).

^e Here and below: not determined due to insolubility of the isolated polymer in THF or DMF.

^f Reaction performed at -20 °C.

^g 0.3 mol% catalyst was used.

Table 2

Polymerization of **12**, **13**, and **15** with catalysts **1** and **2**.^a

Mono- mer	Cat- alyst	Time (h)	Cis, ^b %	Yield, ^c %	M _n ^d kDa	PDI ^d
cycloocta- diene (12)	1	1	10	88	22.9	1.64
	2	36	96	19	99.1	1.60
cyclopent- ene (13)	1	5	15	68	11.1	1.47
	2	3	48	24	102	1.40
<i>trans</i> - cyclooctene (15)	1	1	18	49	— ^e	—
	2	1	70	44	—	—

^a See supporting information for reaction conditions.

^b *cis* content of polymer determined by ¹H NMR and ¹³C NMR spectroscopy.

^c Isolated yield.

^d Determined by MALS GPC.

^e Not determined due to insolubility of the isolated polymer in THF or DMF.